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(71) Applicants
Taiyo Sanso Co. Ltd,

(Incorporated in Japan),

No 1-1 2-Chome Motomachi, Naniwa-ku, Osaka, Japan
Saes Getters S. p. A.,

(Incorporated in Italy),

Via Gallarate, 215/217 Milano, Italy

(72) Inventors
Kiyoshi Nagai,
Claudio Boffito,
Fabrizio Doni,
Marco Succi

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(74) Agent and/or Address for Service
Abel & Imray, Northumberland House, 303-306 High Holborn, London WC1V 7LH

(54) **Superpurifier for argon gas and process for purifying argon gas**

(57) A Superpurifier comprises means for contacting an impurity-containing argon gas with a getter material which is an alloy of zirconium, vanadium and iron which selectively sorbs impurities thereby producing a purified argon gas. The present invention also relates to a method and means for obtaining an argon gas of higher purity than can be obtained by prior purifying processes and apparatus.

Fig.1

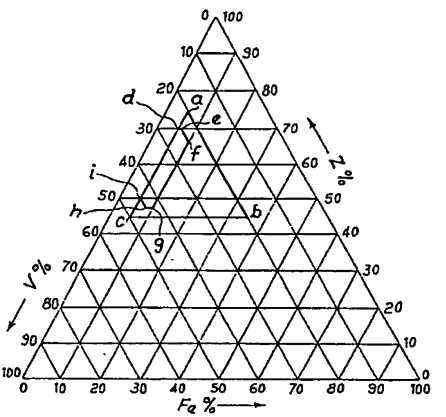

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Fig. 2

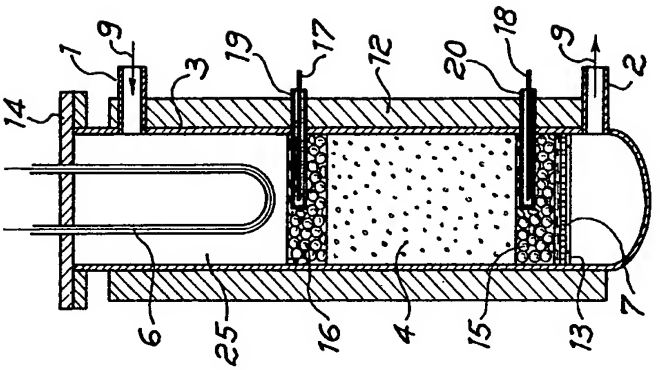


Fig. 1

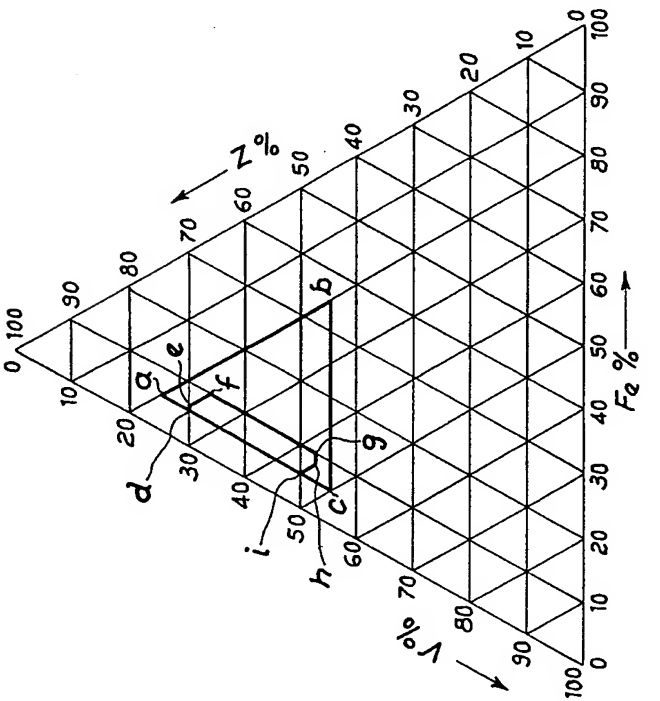


Fig.5

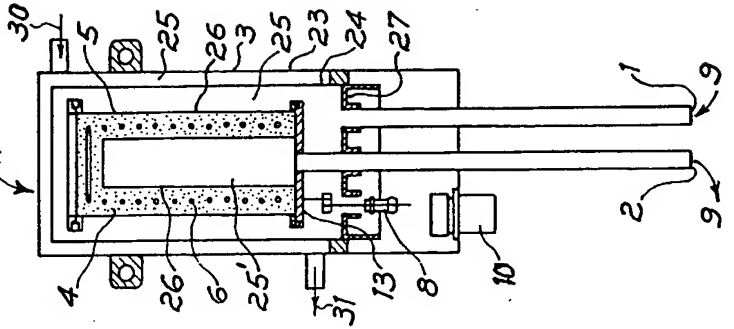


Fig.4

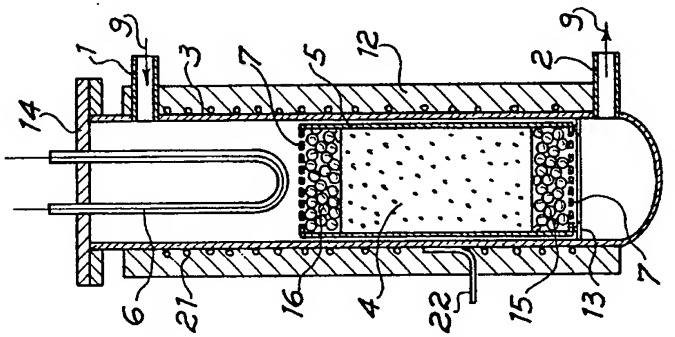


Fig.3

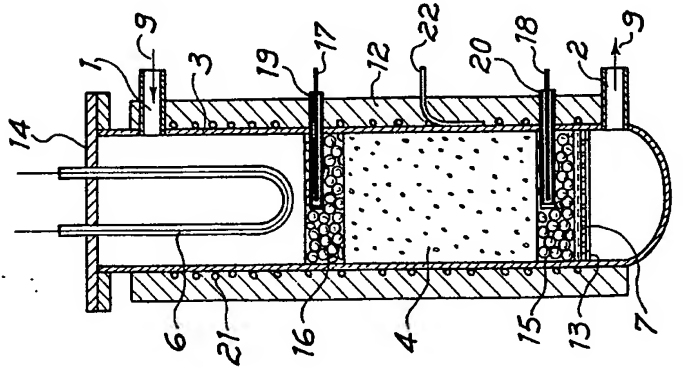
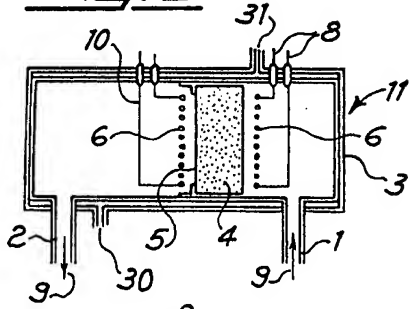


Fig. 6



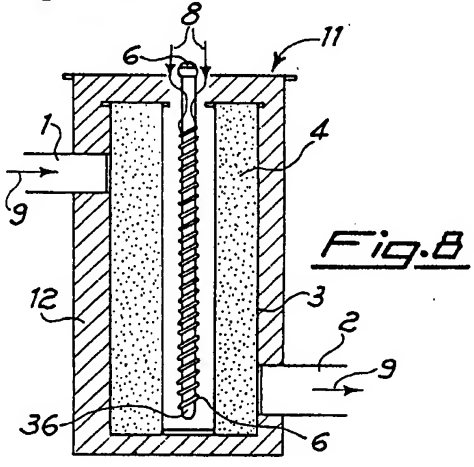


Fig. 8

Fig. 7

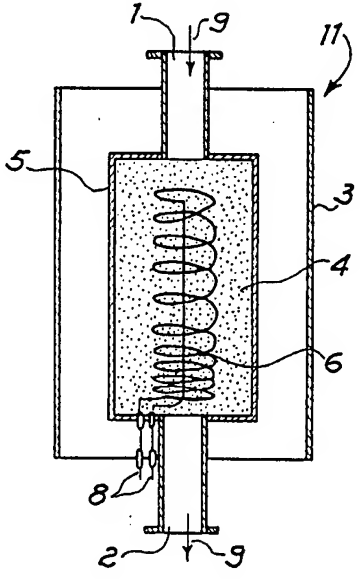
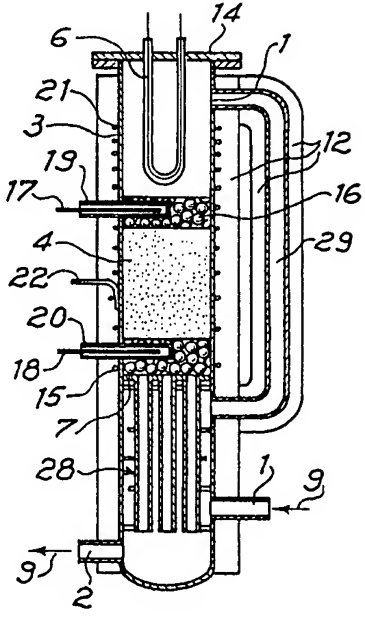


Fig. 9



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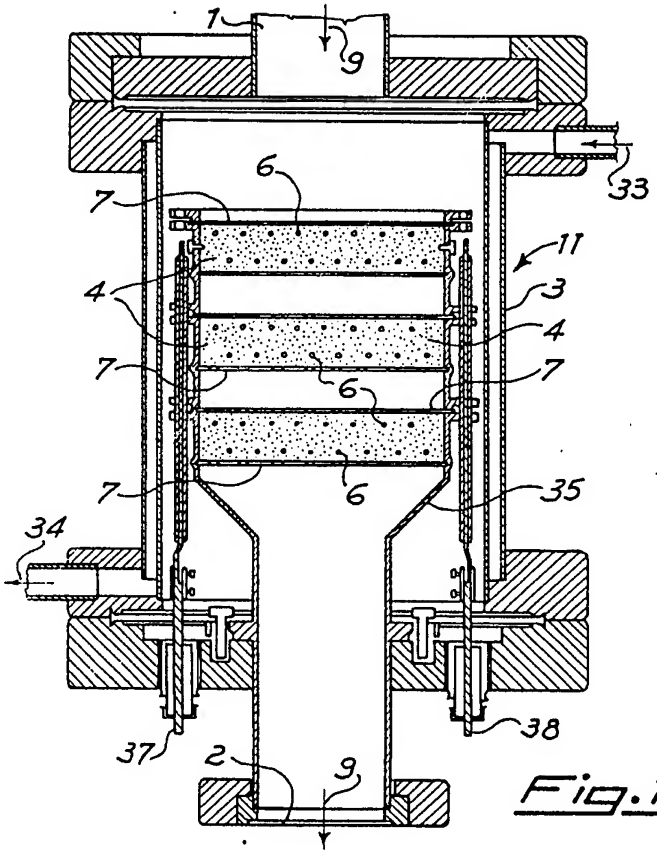

Fig.10

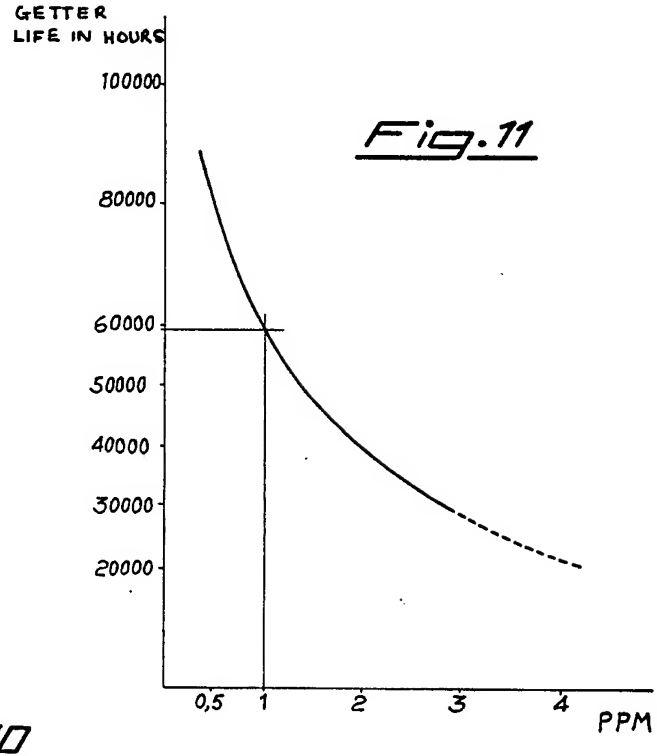

Fig.11

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SPECIFICATION

Superpurifier for argon gas and process for purifying argon gas

Argon, present in air and constituting about one percent of its volume, is separated from nitrogen and oxygen by low-temperature fractional distillation. It is filled either in liquid or gaseous form into cylinders and put on the market.

A high grade inert gas, argon is in wide use to provide atmospheres for heat treatments of metals, for the manufacture of semiconductor substrates and the like. When it is to be employed in superfine microprocessing, it must be further purified by removing impurities to a greater purity immediately before use. For large-volume consumption in industrial processes it is customary to vaporize liquid argon and supply the resulting gas through pipings. Here the problem is how to meet the requirement of rapid and positive removal of the impurities, such as nitrogen, oxygen, hydrogen, carbon dioxide, carbon monoxide, water, methane, and other hydrocarbons, from the gasified argon.

With the view to removing these impurities it has been proposed to combine two steps, that is, passing argon gas through a bed of active charcoal or active alumina or through a molecular sieve of zeolite or the like to eliminate water, carbon dioxide, and hydrocarbons and then contacting the gas with a metallic getter of copper or nickel preheated to a temperature range of 150° to 300°C. Alternatively, the two-step process is followed by an additional step of bringing the gas into pressure contact with a molecular sieve type 5-A under a pressure of 5 to 25 atm. for further purification through removal of residual nitrogen, oxygen, hydrogen, and carbon monoxide. The specification of Japanese Patent Application Public Disclosure No. 107910/1984, which describes the proposed process, also makes clear that argon gas containing the impurities listed in the following table

Constituent	O_2	CO	H_2	N_2	H_2O Dew point
(ppm)	1	100	200	200	60°C

was purified in the foregoing way to a composition as tabled below:

Constituent	O_2	CO	H_2	N_2	H_2O Dew point
(ppm)	1	-	1	20	−72°C

The argon gas purification process disclosed in the afore-mentioned specification of Pat. App. Pub. Discl. No. 107910/1984 is an excellent process for obtaining high-purity argon gas. However, the recent progress of the semiconductor industry suggests that more and more precise microprocessing and hence argon of even higher purity will be required for future production of highly integrated circuits. In fact, there is already strong demand for high-purity argon gas for testing purposes. The technical problem the present invention is intended to solve is lowering the current levels of impurities according to the prior art technology to much lower levels, by two figures in parts per million.

We have intensively studied on the means for purifying argon gas to decrease its impurity concentrations by two orders of magnitude ppm from the usual levels as stated above. As a result, we have discovered a getter that performs even better than the above-mentioned metallic getter of copper or nickel and have arrived at an apparatus and a process capable of most effectively purifying argon gas by the use of the particular getter. The present invention has now been perfected on this basis.

The apparatus according to this invention is a superpurifier for argon gas characterized in that an outer shell is provided with an inlet for argon gas to be purified, an outlet for purified argon gas, at least one getter chamber packed with a getter alloy of zirconium-vanadium-iron system and disposed midway between the two openings, a flow passage so formed that the argon gas that enters the inlet flows through the getter chamber and leaves the outlet, and heater means incorporated into the outer shell to maintain the getter alloy at the temperature at which it functions, the weight composition of the zirconium-vanadium-iron alloy of getter being such that the percentages by weight of the three elements, when plotted in a ternary composition diagram, come within a polygon (Figure 1) having as its corners the points defined by

a. 75%Zr-20%V-5%Fe,
b. 45%Zr-20%V-35%Fe, and
c. 45%Zr-50%V-5%Fe.

The process according to the invention is a process for superpurifying argon gas characterized by the steps of properly dehydrating argon gas to be purified to a moisture content of 1 ppm or less, and then removing impurities by adsorption from the gas of the low moisture content by passing the latter through a getter bed packed with a getter alloy of zirconium-vanadium-iron system maintained at a temperature of 20° to 400°C, said getter alloy having a weight composition such that the percentages by weight of the three elements, when plotted in a ternary composition diagram, come within a polygon (Figure 1) having as its corners the points defined by

a. 75%Zr-20%V-5%Fe,
b. 45%Zr-20%V-35%Fe, and
c. 45%Zr-50%V-5%Fe.

The ternary getter alloy of zirconium, vanadium, and iron to be used in the present invention may be the one described in U.S. Patent Specification No. 4,312,669.

The weight composition that gives a getter of particularly good performance is such that the percentages of weight of the three elements, when plotted in a ternary composition diagram (Figure 1), come within a polygon having as its corners the points defined by

a. 75%Zr-20%V-5%Fe,
b. 45%Zr-20%V-35%Fe, and
c. 45%Zr-50V-5%Fe.

Such a ternary alloy getter characteristically adsorbs moisture and water vapor quantitatively at temperatures in the range of 20° to 400°C, preferably in the range of 200° to 350°C, withot evolving hydrogen, and over a wider temperature range, it adsorbs hydrogen, CO, CO_2, and other gases. These properties have been found advantageously utilizable in the argon gas superpurifier of the invention.

The weight ratio of the elements constituting the ternary alloy getter for use in the superpurifier of the invention may be varied as desired within the range specified above. In any case it is advisable to choose the best possible compositional ratio in view of the getter properties.

The zirconium content in the ternary alloy should not be too high nor too low for otherwise the alloy would tend to evolve hydrogen while adsorbing moisture and also would become plastic creating difficulty to transform into powder.

The vanadium content should not be too low, either, because it would make the alloy unable to exhibit fully satisfactory gas adsorption performance.

On the basis of the iron weight the weight percentage of vanadium is desired to range from 75 to 85%.

The optimum ternary alloy composition of the getter for the superpurifier of the invention may be such that the percentages by weight of the three elements, when plotted in a ternary composition diagram, come within a polygon (Figure 1) having as its corners the points defined by

d. 70%Zr-25V-5%Fe,
e. 70%Zr-24%V-6%Fe,
f. 66%Zr-24%V-10%Fe,
g. 47%Zr-43%V-10%Fe,
h. 47%Zr-45%V-8%Fe, and
i. 50%Zr-45%V-5%Fe.

The process for preparing these alloys is described in the above-mentioned U.S. Patent Specification No. 4,312,669. The products manufactured and marketed by SAES Getters S.p.A. of Milan, Italy, may desirably be used.

It is desirable that the getter alloy be used in the form of an intermetallic compound, which is readily pulverized and can be handled with ease. Moreover, the increased surface area renders the powdered material more active.

The ternary alloy getter is packed in at least one getter chamber provided in a gas flow passage between the inlet for argon gas to be purified and the outlet for purified gas. The packed getter chamber or chambers combine with heater means, installed as an accessory to an outer shell to maintain the getter at its working temperature, to make up an argon gas superpurifier of the invention.

Argon gas to be purified is passed through this superpurifier where it contacts the getter so as to be freed from its impurities by adsorption.

The getter to be packed in the chamber takes the form of pellets in preference to fine particles since the former are easier to provide sufficient interstices therebetween for the gas flow. Also, the getter as pellets of uniform size rather than small lumps irregular in size renders it easy to maintain a constant void ratio in the getter bed, to design the apparatus, and to reproduce the good performance. Thus, while the getter in the form of fine particles or small lumps is not objectionable, the use of pelletized getter, compression molded of the alloy powder, is preferred as it better meets the requirements for industrial designing and manufacture of the argon gas superpurifier.

The heater means to be incorporated in the apparatus of the invention to keep the getter hot enough for the adsorption reaction may take varied forms as will be explained later in connection with preferred embodiments of the invention. The heating method may be electric heating or indirect heating by the use of a heating medium circulated through a double-wall structure or the like. Also, the heating zone may be suitably chosen, for example, in the gas preheating region upstream of the getter bed or chamber, or around or inside the getter mass. Since it is desirable that sufficient heating be done to effect a smooth adsorption reaction of the getter with the gas and produce as uniform a temperature distribution as feasible, the combination of the heating method and zone may be varied, according to the necessity, to best attain the end.

While it is possible that the getter chamber in the apparatus of the invention be provided inside the outer shell, as directly packed in the latter, a preferred arrangement is such that the getter bed consists of at least one cartridge packed with the getter material and which is adapted to be fitted in the outer shell detachably for ease of replacement. The getter components according to this invention adsorb and

remove impurities from impure argon gas by chemical adsorption that involves chemical changes. They therefore are consumed stoichiometrically and have a limited life. After service for a predetermined period the getter must be replaced by fresh one; otherwise the purpose of superpurifying argon gas will no longer be achieved. To this end the superpurifier including the outer shell packed with the getter may be handled as a single unit and replaced as such from time to time. It is also possible to fill up the getter in a cartridge instead and dismount the cartridge from the outer shell for replacement at proper intervals of time. The cartridge type is more practical with larger-size equipment.

The cartridge desirably employs a metal case so perforated as to facilitate the gas flow.

Because the superpurifier of the invention is intended to purify argon gas until the concentrations of its ingredients as impurities are reduced to 0.01 ppm or less each, it is advisable that the inner wall portion of the apparatus with which the purified gas emerging from the getter chamber comes in contact be made of a metal polished on the surface to be close-grained and smooth enough to minimize gas adsorption and which does not form powder due to corrosion. Such metals include, for example, but are not limited to, stainless steels and proprietary alloys such as Hastelloy, Incoloy, and Monel metal. Any other metal material which satisfies the above requirements may be suitably chosen and used. The chosen metal may be "baked", or heat treated, before use to reduce the volume of subsequent gas release from the metal material itself.

As stated above, the inner wall material of the apparatus that contacts the purified argon gas is desired to have a densely and smoothly polished surface to minimize gas adsorption. The desirable degree of smoothness of the polished surface is numerically defined to be such that the roughness of the inner wall surface to contact argon gas is 0.5 μm or less preferably 0.25 μm or less in terms of the centerline average height (R_a) [Japanese Industrial Standard (JIS) B 0601-1970]. This numerical range is not always critical but is recommended as a dependable, safe range.

Although the polished inner wall material is advantageously used in the zone where the gas flowing out of the cartridge chamber comes in contact, it is, of course, possible to use it also in the zone where the gas passing through the cartridge contacts. In many cases it is rather inconvenient to use the polished material only in the zone where the gas that has flowed past the cartridge contacts. The surface polishing and baking will markedly shorten the time period required before highly purified gas begins to be obtained at a constant rate, even from a new apparatus.

In the apparatus of the present invention the means for solving the technical problem can be variously embodied as suggested above. Thus it is to be understood that the invention is not limited to the specific embodiments thereof so far described but various modifications may be made without departing from the spirit and scope of the invention.

Dehydration in the process of the invention is done on the following grounds. The moisture content in impure argon gas usually is by far the higher than the levels of other impurities. When special weight is placed on moisture removal, the getter life and therefore the service life of the argon gas superpurifier will be remarkably extended or, stated differently, a striking increase in the volume of purified argon gas will be realized. Any known dehydration technique may be adopted provided it does not obstruct the practice of the present invention. For example, the dehydration may be by adsorption with a molecular sieve of synthetic zeolite or the like, with alumina gel, or with phosphorus pentoxide, or by freezing at a cryogenic temperature below −160°C, or by adsorption with silica gel, active charcoal, or other adsorbent at low temperature below −40°C. Figure 11 shows the relation between the moisture content in the gas to be purified and the getter life. When the gas has a large moisture content, it is dehydrated before superpurification, preferably to a moisture content of 1 ppm or less.

In order to control the moisture content within the range of 1 ppm or less, the system is designed for operation as follows. Using a moisture meter capable of continuously making trace moisture content measurement, the moisture level in the dehydrated argon gas is automatically monitored. When the moisture content in the argon following the dehydration has gradually risen near 1 ppm, the dehydrator is switched on before the 1 ppm level is reached, so that the moisture content in the argon gas before entering the getter bed is kept within the range of 1 ppm or less. Analyzers suited for such continuous, automatic measurement of trace moisture contents are, for example, moisture meters manufactured by Endress und Hauser GmbH of West Germany and marketed under the trade designations "ENDRESS-HAUSER HYGROLOG, WMY 170" AND "- WMY 370", products tradenamed "PANAMETRICS Hygrometer, Model 2100", "- Model 700", and "- System I" by Panametrics Inc. of the U.S., and another American product "Du Pont 510 Moisture Analyzer" by E.I. Du Pont de Nemours & Co. Other analyzers of performance comparable to or better than the above may, of course, be employed instead.

Such a moisture meter may also be used for the measurement and monitoring of the moisture content in the argon gas after purification. The results of analysis are utilized as data indicative of decreasing adsorbability of the getter and for the decision on timing of any switchover of the superpurifier operation or of replacement of the getter-filled cartridge.

For the detection and determination of trace impurities other than moisture in argon gas, an analyzer for ultramicro amounts of gases (mass-filter type mass spectrometer for high-sensitivity continuous analysis) manufactured by Nichiden-ANELVA Corporation (in Japan) under the trade designation "TE-360B" may be used. The analytical values are utilized as a measure of declining performance of the getter and for the decision on timing for the switchover of the superpurifier operation or replacement of the getter

cartridge.

As regards those analytical values, it is advisable to set up a purification system so that, whenever any of prefixed upper limits or levels of individual impurities is reached, a switchover in operation is automatically accomplished as scheduled. Such a system will ensure high quality of the final argon gas.

In order that the impurities be removed from the dehydrated argon gas by passage through and adsorption by the getter bed of zirconium-vanadium-iron alloy, the reaction temperature is kept in the range of 20° to 400°C. At a temperature below 20°C, the impurities are adsorbed by the getter surface but cannot be expected to diffuse into the getter mass. Thus the adsorption practically comes to an end in the state of saturation on the surface, without fully making use of the getter capacity. In the specified range of 20° to 400°C the getter performs adsorption to the full, allowing the impurities to diffuse thoroughly therein. The apparent life of the getter is accordingly extended.

On the other hand, in the temperature region above 400°C, the hydrogen once adsorbed by the getter can be desorbed because it has an equilibrium adsorption pressure higher than those of other impurities. Setting a reaction temperature in excess of 400°C is therefore undesirable.

Among the specified temperature range of 20° to 400°C, a narrower range of 220° to 380°C is most preferred. A temperature in the latter range is the most recommended reaction temperature in that it assures a high adsorption rate and thorough diffusion of the impurities into the bed of getter with no possibility of hydrogen desorption.

The argon gas superpurifier of the present invention is suited for superpurifying the conventionally purified argon gas to an even higher purity. It can purify argon gas by passage therethrough to lower the concentrations of impurities in the feed, such as oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen (N_2), hydrogen (H_2), methane (CH_4), and water (H_2O), down to 0.01 ppm or less each. Thus it realizes superpurification of argon gas to such a high purity that none of existing purifiers have ever achieved.

Moreover, the life of getter used in the argon gas super-purifier of the invention can be markedly extended and the volume of argon gas purification greatly increased by first decreasing the moisture content in the impure argon gas to 1 ppm or less by proper dehydration in accordance with the process of the invention and then passing the dehydrated gas through the superpurifier of the invention.

The present invention will now be described in more detail below, by way of example only, in connection with embodiments thereof.

Argon gas superpurifiers embodying the invention are illustrated in Figures 2 through 10. Figure 2 shows an argon gas superpurifier comprising: an outer shell 3 made of a stainless steel tube (grade SUS 304 TP conforming to Japanese Industrial Standard JIS G 3448) which has an argon gas inlet 1 formed near the top and an argon gas outlet 2 near the bottom, the shell being covered with a heat insulator 12 all over the surface; a top cover 14 fitted to the top of the outer shell 3; a heater 6 inserted through the top cover 14 into the space 25 inside the shell; a bed of getter 4 packed in the space defined below the heater 6 between upper and lower buffers 16, 16; and a perforated plate 7 held by a support 13 which in turn is secured to the inner wall of the outer shell and is supporting the bed as well as the perforated plate. The getter used was a ternary alloy getter of zirconium (68-72 wt%), vanadium (24-25 wt%), and iron (5-6 wt%) manufactured and marketed by SAES Getters S.p.A., Type No. "St 707" in the form of columnar pellets having a diameter of 3 mm and height of 4 mm.

The buffers, indicated at 15, 16, consist of a layer each of small alumina spheres 4 mm in diameter packed up to a height of about 5 cm. They correct any ununiform flow of the gas through the getter bed, keep the fine particles of the getter from scattering, and uniformalize the temperature distribution.

While the embodiment being described use small alumina spheres in forming the buffers, small stainless steel balls or a stack of fine-mesh stainless steel screens may be employed instead. Also, the buffers are not always used, and a buffer-less embodiment will be described later.

In the upper portions of the buffers 15, 16 are embedded sheathes 20, 19 accommodating thermometers 18, 17, respectively. Chromel-Alumel thermocouples are used as the thermometers.

Argon gas 9 to be purified is introduced into the vessel at the inlet 1, heated by the heater 6, passes through the upper buffer 16 and thence, as a uniform flow, through the bed of getter 4 where it is freed from impure gas contents by adsorption. The purified gas is led through the perforated plate 7 and taken out of the vessel at the outlet 2.

Figure 3 and following figures show other embodiments of the invention. Throughout these figures like parts are designated by like numerals and the description is omitted or minimized each.

Figure 3 shows a superpurifier of the same construction as the embodiment in Figure 2 excepting that an electric heater 21 is coiled round the outer shell 3 and a thermocouple 22 is installed to measure the heater temperature. This modification facilitates the temperature control of the getter bed.

Although Figures 2 and 3 illustrate the embodiments in which the bed of getter 4 is directly packed in the outer shell 3, the getter bed may be separately provided as well. Figure 4 shows an arrangement of cartridge 5 where the getter 4 and buffers 15, 16 are accommodated in a cylinder equipped with perforated plates 7 at both ends. After service for a given period, the cartridge 5 may be taken out by removing the top cover 14 and replaced by a new one. This permits more efficient operation than with the arrangements of Figures 2 and 3.

Figure 5 shows another embodiment 11, in which the outer shell 3 is of a double-wall construction,

consisting of an inner wall 24 and an outer wall 23. The space between the walls provides a passage through which a heating medium such as steam flows from a heating medium inlet 30 to an outlet 31. A coolant may be passed instead of heating medium depending on the case. In the space defined by the inner wall is accommodated a cartridge 5 containing a getter 4, with a coil of electric heater 6 embedded in the getter. The heater 6 is connected to an external power source not shown through leads 8 (only one of them being shown) and a terminal assembly 10. The cartridge 5 has inner and outer porous walls 26 concentrically held in spaced relation by a support 13. The inner wall 24 of the outer shell is abutted at its lower end against a bottom plate with a flange 27, through which a gas inlet pipe 1 and an outlet pipe 2 extend. The pipe 2 serves also to support the cartridge 5. Argon gas 9 to be purified is fed through the inlet 1 into the outer space 25, heated thereto a proper temperature, and thence forced through the porous wall 26 into the getter layer 4 for purification. The purified gas flows out into the inner space 25' and taken out via the outlet 2.

Figure 6 shows still another embodiment of superpurifier 11. The outer shell 3 is again of double-wall construction, with a space formed therein to circulate a heating medium introduced at an inlet 30 and discharged at an outlet 31 to perform temperature control. Inside the inner wall is disposed a cartridge 5 packed with a getter 4 between perforated plates. On both sides of the cartridge are arranged heaters 6 which are connected to external power sources through leads 8. Impure argon gas 9 is fed at an inlet 1, preheated by the heating medium, purified by passage through the getter mass 4 kept at a given temperature by the heaters 6, and then taken out at an outlet 2.

Yet another embodiment of superpurifier 11 is shown in Figure 7. A cylindrical outer shell 3 supports a cartridge 5 by means of upper and lower plates (not shown). The cartridge 5 comprises a built-in electric heater 6 with leads 8 and a mass of getter 4 filled in the space between upper and lower perforated plates or buffer layers, with the heater embedded therein.

Figure 8 shows another apparatus 11 embodying the invention. An inner cylinder is provided inside an outer shell 3 which consists of inner and outer walls and a heat insulator 12 filling up the space between the walls. A getter 4 is packed in the space between the inner cylinder and the outer shell, and an electric heater 6 coiled round a ceramic rod 36 is inserted into the central space in the inner cylinder. Argon gas 9 to be purified enters the vessel at an inlet 1, passes through the getter 4, and the purified gas leaves the vessel at an outlet 2.

Figure 9 shows another embodiment, which is a modification of the superpurifier illustrated in Figure 4 and is characterized by means for recovering the heat of purified argon. Argon gas 9 to be purified enters a heat exchanger 28 installed under the purifier body, undergoes heat exchange with the outgoing gas, and the gas so preheated moves through a pipe 29 surrounded by a heat insulator 12 and through an upper inlet 1 into a bed of getter 4. The purified gas is cooled in the heat exchanger and leaves the purifier at an outlet 2.

Figure 10 shows a further embodiment. The outer shell 3 is a double-wall cylinder, and a heating medium is introduced into the space between the walls at an inlet 33 and is discharged at an outlet 34. Inside the outer shell 3 is disposed a gas-tight cartridge 35. The space in the cartridge case is partitioned horizontally with a plurality of perforated plates 7, and a plurality of getter beds 4 are formed, each filling up the space formed by every other pair of the perforated plates. The getter beds have electric heaters 6 embedded therein, one for each, and supplied with electricity through leads 37, 38. Argon gas 9 to be purified flows in at an inlet 1 and the purified gas flows out at an outlet 2.

Examples of the invention which used a specific getter composition will now be explained.

The instruments used for gas analyses in the examples were as follows:

Gas analysis instrument:
Gas chromatograph-mass spectrometer, Model TE-360B (mfd. by Anelva Corp.)

Moisture meter:
Hygrometer, Model 700
(mfd. by Panametric Co.)

Surface roughness meter:
Surfcorder, Model SE-3H
(mfd. by Kosaka Laboratory Co., Ltd.)

Example 1

A powdered non-evaporable getter alloy having a weight composition of 70%Zr-24.6%V-5.4%Fe and a particle size of between 50 and 250 μm is placed in the superpurifier for argon gas shown in Figure 2. The stainless steel (SUS 304) cylinder has an outside diameter of 21.7 mm and an inside diameter of 17.5 mm, its length being 350 mm. The length of cylinder occupied by the getter material, including the heights, 5 mm each, of the upper and lower buffers of alumina spheres, (bed height) is 200 mm. Impure argon is introduced into the superpurifier at a temperature of 25°C and a pressure of 6 kg/cm² (gauge) at a flow rate of 0.6 ℓ/min. The argon flows through the non-evaporable getter bed held at 350°C and issues at a pressure of 4 kg/cm² (gauge) from the outlet where its impurity level is measured for various gases. This impurity level is measured 40 min after the start of the flow of argon.

TABLE I

Gas	*Inlet impurity level (ppm)*	*Outlet impurity level (ppm)*
O_2	0.4	0.006
N_2	0.5	0.011
CH_4	0.06	0.007
CO	0.07	0.002
CO_2	0.04	0.002
H_2O	5.0	no trace

The level of impurities in the outlet gas remains constant for 930 hours.

Example 2

Pellets were produced having a diameter of 3 mm and height of 4 mm by compression of a non-evaporable getter alloy having a composition and particle size identical to those of the getter alloy of Example 1. The pellets were loaded into the super-purifier shown in Figure 3. The stainless steel (SUS 304) cylinder had an outer diameter of 89.1 mm and an inner diameter of 83.1 mm. Its length was 660 mm. The length of the cylinder occupied by the pellets of getter material, including the thicknesses of the upper and lower buffers (of alumina spheres) each having a bed height of 5 mm, was 185 mm. Impure argon was introduced into the superpurifier at a temperature of 25°C and a pressure of 4 kg/cm² (gauge) at a flow rate of 12 ℓ/min.

The impure argon flowed through the non-evaporable getter bed held at a temperature of 350°C by means of a spiral resistance heater and issued at a pressure of 3.95 kg/cm² (gauge) from the outlet while its impurity level was measured for various gases. The impurity level was measured 40 min after the start of the flow of argon. The results obtained were as shown in Table II.

TABLE II

Gas	Inlet impurity level (ppm)	Outlet impurity level (ppm)
O_2	6.0	0.01
N_2	7.5	0.02
CH_4	2.0*	0.009
CO	9.5	0.003
CO_2	6.3	0.003
H_2O	5.0	no trace

* The methane impurity level was obtained by deliberately adding CH_4 to the inlet gas. The level of the impurities in the outlet gas remained constant for 930 hours.

Example 3

In this example the procedure of Example 2 was repeated in all respects except that the H_2O impurity level was 1 ppm and not 5 ppm.

Table III shows the results.

TABLE III

Gas	Inlet impurity level (ppm)	Outlet impurity level (ppm)
O_2	6.0	0.01
N_2	7.5	0.02
CH_4	2.0	0.009
CO	9.5	0.003
CO_2	6.3	0.003
H_2O	1.0	no trace

* The methane impurity level was obtained by deliberately adding CH_4 to the inlet gas.
The level of the impurities in the outlet gas remained constant for 2670 hours.

Example 4

Pellets were produced exactly as in Example 2 and placed in the cartridge shown in Figure 4. The cartridge had an outside diameter of 80 mm, an inside diameter of 78 mm, and length of 244 mm. The same mass of pellets was used as in Example 2. The cartridge was then placed in a cylinder identical to that of Example 2 (except that its length was 719 mm). Impure argon was caused to flow through the superpurifier at the same inlet pressure, temperature, and flow rate as described in Example 2. The cartridge was maintained at 350°C. The outlet gas pressure and composition were found to be identical to those found in Example 2 at the point 40 min after the start of the flow of argon. The level of the impurities in the outlet gas again remained constant for 930 hours.

Example 5

In this example the procedure of Example 2 was followed in all respects except that the inner surface roughness of the cylinder was R_a = 0.5 μm (normally R_a = 2.5 μm) and the stainless steel outlet piping (outside diameter 9.5 mm and inside diameter 7.5 mm) had an inner surface roughness of R_a = 0.2 μm. The results shown in Table IV were obtained 40 min after the start of the flow of argon.

TABLE IV

Gas	Inlet impurity level (ppm)	Outlet impurity level (ppm)
O_2	6.0	0.003
N_2	7.5	0.002
CH_4	2.0	0.009
CO	9.5	0.003
CO_2	6.3	0.003
H_2O	5.0	no trace

The level of the impurities in the outlet gas remained constant for 930 hours.

Example 6

In this example the procedure of Example 5 was followed in all respects except that the water vapor content of the argon gas to be purified was reduced to below 0.6 ppm by first passing it through a dryer bed consisting of a stainless steel (SUS 304) cylinder having an outside diameter of 89.1 mm, inside diameter of 83.1 mm, and length of 830 mm filled to a bed height of 500 mm with a molecular sieve type 5-A. The outlet pressure from the dryer bed and therefore the inlet pressure to the superpurifier was found to be 3.7 kg/cm² (gauge) and the super-purifier outlet pressure was 3.7 kg/cm² (gauge). This impurity level was measured 40 min after the start of the flow of argon.

The results were as shown in Table V.

TABLE V

Gas	Inlet impurity level (ppm)	Outlet impurity level (ppm)
O_2	6.0	0.003
N_2	7.5	0.002
CH_4	2.0	0.009
CO	9.5	0.003
CO_2	6.3	0.003
H_2O	0.6	no trace

The level of the impurities in the outlet gas remained constant for 2670 hours.

The procedure of Example 6 was repeated except that the temperature was varied to see the effects of different getter temperatures. The results are given in Table VI.

TABLE VI

Inlet impurity level	*(ppm)*	*Outlet impurity level (ppm) at temperature 20°C*	*200°C*	*350°C*	*400°C*
O_2	6.0	0.003	0.003	0.003	0.003
N_2	7.5	0.002	0.002	0.002	0.002
CH_4	2.0	2.0	0.2	0.009	0.006
CO	9.5	0.003	0.003	0.003	0.003
CO_2	6.3	0.003	0.003	0.003	0.003
H_2O	0.6	no trace	no trace	no trace	no trace
Outlet gas remained constant for		30 hr	390 hr	2670 hr	2900 hr
Power consumption		0	0.56 kW/h	1.04 kW/h	1.2 kW/h

The table indicates that excellent effects were achieved in the temperature range of 20° to 400°C, especially in the range of 200° to 400°C.

Examples 7, 8, 9 and 10

Pellets were produced having a diameter of 3 mm and a length of 4 mm by compression of non-evaporable getter powders having weight composition indicated in the following Table and having particle sizes of 50 - 250 μm (150 μm in average). These pellets were loaded into a superpurifier having the same construction in the same manner as Example 2. Argon gas containing impurities was introduced into the superpurifier at a temperature of 25°C, inlet pressure of 4 kg/cm² (gauge) and a flow rate of 12 l/min.

The impurity-containing argon gas was passed through the bed of the non-evaporable getter kept at a temperature of 350°C by means of a spiral resistance heater and emerged from the outlet at a pressure of 3.95 kg/cm² (gauge). The impurity level was measured 40 min after the start of the flow of argon and the results in Table VII were obtained.

TABLE VII

		Ex.7	*Ex.8*	*Ex.9*	*Ex.10*
Getter alloy comp.	Zr(%)	65	48	46	46
	V (%)	25	44	21	37
	Fe(%)	10	8	33	17
Gas	Inlet imp. (ppm)	Outlet impurities (ppm)			
O_2	6.0	0.01	0.01	0.02	0.03
N_2	7.5	0.02	0.02	0.02	0.02
CH_4	2.0	0.006	0.01	0.01	0.01
CO	9.5	0.003	0.003	0.008	0.005
CO_2	6.3	0.003	0.003	0.006	0.006
H_2O	5.0	no trace	no trace	no trace	no trace
Period of time for which outlet impurity was constant (hrs)		780	530	900	810

The outlet impurity levels were constant for the length of time indicated in the table.

4. Brief description of the drawings:

Figure 1 is a ternary composition diagram of the getter alloy for use in the present invention;

Figures 2 through *10* are vertical sectional views of varied embodiments of the apparatus according to the invention; and

Figure 11 is a graph indicating the relation between the moisture content in argon gas and the getter life.

CLAIMS

1. A superpurifier for argon gas characterized in that an outer shell is provided with an inlet for argon gas to be purified, an outlet for purified argon gas, at least one getter chamber containing a getter alloy of zirconium-vanadium-iron system and disposed between the two openings, a flow passage so formed that the argon gas that enters the inlet flows through the getter chamber and leaves the outlet, and heater means to maintain the getter alloy at the temperature at which it functions, the weight composition of the zirconium-vanadium-iron alloy of getter being such that the percentages by weight of the three elements, when plotted in a ternary composition diagram, come within a polygon having as its corners the points defined by

a. 75%Zr-20%V-5%Fe,
b. 45%Zr-20%V-35%Fe, and
c. 45%Zr-50%V-5%Fe.

2. A superpurifier as defined in claim 1 characterized in that said getter alloy to be used in said getter chamber is in the form of pellets made by compressing and pelletizing a powdered Zr-V-Fe alloy.

3. A superpurifier as defined in claim 1 characterized in that the weight composition of said getter alloy is such that the percentages by weight of the three elements, when plotted in a ternary composition diagram, come within a polygon having as its corners the points defined by

d. 70%Zr-25%V-5%Fe,
e. 70%Zr-24%V-6%Fe,
f. 66%Zr-24%V-10%Fe,
g. 47%Zr-43%V-10%Fe,
h. 47%Zr-45%V-8%Fe, and
i. 50%Zr-45%V-5%Fe.

4. A superpurifier as defined in claim 1 characterized in that said getter chamber comprises at least one cartridge packed with said getter alloy, and that said cartridge is detachably installed in said outer shell so that it can be easily replaced by new one.

5. A superpurifier as defined in claim 4 characterized in that each said cartridge comprises a perforated metal container packed with said getter alloy.

6. A superpurifier as defined in claim 1 characterized in that the apparatus material with which the argon gas purified by the flow through said getter chamber comes in contact is such that the inner wall surface to contact the gas has been polished to a surface roughness (R_a) of 0.5 μm or less in terms of the centerline averge height [in conformity with the Japanese Industrial Standard (JIS) B 0601-1970].

7. A process for superpurifying argon gas characterized by the steps of dehydrating argon gas to be purified to a moisture content of 1 ppm or less, and then passing the gas of the low moisture content through a getter bed containing a getter alloy of zirconium-vanadium-iron system maintained at a temperature of 20° to 400°C, said getter alloy having a weight composition such that the percentages by weight of the three elements, when plotted in a ternary composition diagram, come within a polygon (Figure 1) having as its corners the points defined by

a. 75%Zr-20%V-5%Fe,
b. 45%Zr-20%V-35%Fe, and
c. 45%Zr-50%V-5%Fe.

8. A process as defined in claim 7 characterized in that the argon gas of the low moisture content is flown through said getter alloy bed maintained at a temperature of 220° to 380°C.

9. A superpurifier for purifying an impurity-containing argon gas, said superpurifier comprising:

A. an outer shell having a gas inlet and a gas outlet;

B. a gas flow passage within the outer shell extending from the gas inlet to the gas outlet and providing fluid communication therebetween;

C. a getter chamber provided in the gas flow passage, said getter chamber being disposed between the gas inlet and the gas outlet;

D. a getter material provided within the getter chamber, said getter material being a zirconium-vanadium-iron alloy having a composition which, when plotted on a ternary composition diagram in weight percent Zr, weight percent V and weight percent Fe, lies within a polygon having as its corners the points defined by:

a. 75%Zr-20%V-5%Fe
b. 45%Zr-20%V-35%Fe, and
c. 45%Zr-50%V-5%Fe, and

E. means for heating the getter material and maintaining the getter material at a temperature at which the getter material selectively sorbs impurities from an impurity-containing argon gas.

10. The superpurifier of Claim 9 wherein the getter material is a zirconium-vanadium-iron alloy having a composition which, when plotted on a ternary composition diagram in weight percent Zr, weight percent V and weight percent Fe, lies within a polygon having as its corners the points defined by:

d. 70%Zr-25%V-5%Fe,
e. 70%Zr-24%V-6%Fe,
f. 66%Zr-24%V-10%Fe,
g. 47%Zr-43%V-10%Fe,
h. 47%Zr-45%V-8%Fe, and
i. 50%Zr-45%V-5%Fe.

11. A process for superpurifying an impurity-containing argon gas having a moisture content of 1 ppm or less, said process comprising the steps of:

I. providing a superpurifier comprising:

A. an outer shell having a gas inlet and a gas outlet;

B. a gas flow passage within the outer shell extending from the gas inlet to the gas outlet and providing fluid communication therebetween;

C. a getter chamber provided in the gas flow passage, said getter chamber being disposed between the gas inlet and the gas outlet;

D. a getter material provided within the getter chamber, said getter material being a zirconium-vanadium-iron alloy having a composition which, when plotted on a ternary composition diagram in weight percent Zr, weight percent V and weight percent Fe, lies within a polygon having as its corners the point defined by:

a. 75%Zr-20%V-5%Fe,
b. 45%Zr-20%V-35%Fe, and
c. 45%Zr-50%V-5%Fe, and

E. means for heating the getter material and maintaining the getter material at a temperature at which the getter material selectively sorbs impurities from an impurity-containing argon gas; and

II. maintaining the getter material at a temperature of 200° to 350°C; and

III. introducing the impurity-containing argon gas into the outer shell of the superpurifier through the gas inletåd

IV. contacting the impurity-containing argon gas with the getter material in the superpurifier thereby sorbing impurities from the impurity-containing argon gas to produce a purified argon gas; and

V. collecting the purified argon gas which exits the superpurifier through the gas outlet.

12. A process for purifying argon comprising passing argon gas through a getter bed containing a getter alloy as specified in claim 7 at a temperature of 20° to 400°C.

13. A superpurifier for argon constructed substantially as described herein with reference to, and as illustrated by, any one of Figures 2 to 10 of the accompanying drawings, the superpurifier containing a getter as specified in claim 1.

14. A process for purifying argon carried out substantially as described in any one of the Examples herein.

15. Argon whenever purified using apparatus as claimed in any one of claims 1 to 6, 9, 10 and 12.

16. Argon whenever purified by a process as claimed in any one of claims 7, 8, 11 and 13.

17. Any novel feature or any novel combination of features described herein.

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